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A Study on Evaluating the Comparative Effect of Citrus Peels (*Citrus medica linn, Citrus limon, Citrus limetta*) on Tannery Effluent

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Abstract

The present study investigated the comparative effect of citrus peels *(Citrus medica linn, Citrus limon, Citrus limetta)* on tannery effluent. The Rapid industrialization has resulted in the contamination due to toxic pollutants, which is a challenging problem for environment. The biological way of treatment was focussed in the present study. The citrus peels discarded as waste, were used as the bio adsorbents for the adsorption of impurities from tannery effluent. The dried and powdered peels of citrus such as *Citrus medica linn, Citrus limon, Citrus limetta peel powder, peel powder were used* in 0.5, 3.0, 5.5, 8.0, 10.5 g/100ml and used for treatment of tannery effluent. The physical and chemical parameters of the tannery effluent were determined before and after treatment with 3 varieties of citrus peels. It was noticed that at concentration 10.5 g/100ml in *citrus limon*, a good reduction in the level of physical and chemical parameters were seen which indicated the success of treatment process. Finally, IF-IR was performed to identify the active component responsible in treatment process.

Keywords

Adsorption, *Citrus limon*, Chromium, Tannery effluent.

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1. INTRODUCTION:

Water is undoubtedly the most vital element for the natural resources. It is essential not only for survival but also contributes to the quality of our lives. The worldwide water demand is increasing day by day and in many developing countries, access to clean and safe water is a crucial issue. Our society Generates waste water in different sector, industry, agriculture, mining, energy, transportation, construction and consumers but untreated tanneries cause environmental pollution to a great extent. Throughout the world, the waste generated by the process of leather tanning is huge. It is considered as one of the most polluted industrial wastes, because the untreated release of tannery effluents contains high amount of metals and nitrogenous compounds such as organic matter, sulphides and chromium, considered to be toxic to plants, animals and soil (Akpomic, 2013). Toxins from these industrial wastes are also leaching in to the ground water and the chemicals end up in forming coloured ponds and lakes in residential areas that are causing much harm (SH.Tinni *et al*., 2014).

So, there is a need to remove the heavy metals from the wastewater before discharging in to the environment. Cost effectiveness and technical applicability are the two important key factors for selecting effective low-cost adsorbent for heavy

metals removal. The technologies like electro floatation, electro kinetic cautions and coagulation combined with electro flotation and filtrations. Ion exchange, chemical precipitation, carbon adsorption and membrane technologies are very costly and also having many disposal problems. (Namasivayam *et al*., 1997).

Therefore, the most important challenges that scientist all over the world are facing is the treatment of tannery waste water to make it reusable and more efficient. The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient (Nitin W Ingole *et al*., 2013). So, there was a necessary to search for alternative technologies to remove toxic metals from wastewater has focused attention on "bio sorption" which depends on metal binding property to various biological materials.

The use of agricultural waste (Natural Coagulants) is one of the rich sources of low-cost adsorbents in the water treatment were focused as an alternative to the expensive chemical coagulants. The purpose of this research is to determine the effect of citrus peel on tannery effluent. This research work may create better awareness to all tanneries which are discharging effluents in large amount without considering an appropriate treatment method before discharging wastewater to the environment (Akilu Asfaw *et al*., 2012).

Treatments of Tannery Effluent using Citrus Peel Waste:

Lemon peel waste works as a low-cost natural coagulant which is (i) able to remove turbidity from tannery effluent (ii) replace the synthetic chemical coagulant (iii) act as a significant environment friendly product. Bitter lime (*Citrus medica linn*), Lemon (*Citrus limon*) and sweet lime (*Citrus limetta*) is under the category of citrus species of the family Rutaceae. The citrus industry produces lot of waste mainly in the form of peel, which account 50% of the total fruit weight (M. Imran *et al*., 2016). These peels can be used for the purpose of bio sorption which contains functional groups and increases the adsorption capacity of the bio waste (Doke and khan, 2017). In the present study, an attempt was made to assess the physio chemical characteristics of tannery effluent before and after treatment using peels of *citrus medica linn, Citrus limon and citrus limetta*.

MATERIALS AND METHODS:

Collection of Tannery Effluent:

The Tannery Effluent was collected from Ambur generated as waste from tannery industry. The sample was collected in a sterilized bottle.

Collection and Preparation of *Citrus medica linn, Citrus limon, Citrus limetta*

The peels of *Citrus medica linn, Citrus limon, Citrus limetta* was collected from the local market and washed thoroughly in tap water for 2- 3 times. After that it was subjected to drying in sunlight for 4-5 days. The sample weight was recorded before and after drying and transferred in to sterilized bags.

Determination of moisture content:

The formula for calculating moisture content was

$$\text{Moisture content} = \frac{wet\ weight - dry\ weight}{wet\ weight} \times 100$$

Physical chemical characteristics of tannery effluent:

The various physical chemical characteristics such as Colour, Odour, Total hardness, pH, Total Suspended Solids, Total Dissolved Solids, Chemical Oxygen Demand, Biological Oxygen Demand, Calcium, Magnesium, Chloride, Sodium, Sulphate, Chromium, Oil and grease was noticed at different concentrations.

TREATMENT OF TANNERY EFFLUENT:

- Each Lemon peel powder (*Citrus medica linn, Citrus limon, Citrus limetta*) was taken in different concentration as 0.5, 3.0, 5.5, 8.0, 10.5g/100ml of tannery effluent in each conical flask and the samples were incubated at 37°C for 24 hours in Rotatory Shaker.
- At different intervals pH of the incubated tannery sample was noted. After the period of incubation, samples were filtered using filter paper and the supernatant was subjected to physical and chemical parameters.

FT-IR ANALYSIS:

To identify the functional groups, present in the citrus peels (*Citrus medica linn, Citrus limon, Citrus limetta*) involved in adsorption of chemical from tannery effluent samples were subjected to FT-IR analysis in the range of 400-4000 cm^{-1}.

4. RESULTS AND DISCUSSION:

In the present study **"A STUDY ON EVALUATING THE COMPARATIVE EFFECT OF CITRUS PEELS (*Citrus medica linn, Citrus limon, Citrus limetta*) ON TANNERY EFFLUENT"** the pertaining results were obtained and interpreted.

Tannery industry is reputed globally as a major industry and contribute serious environmental problem. Treatment of the contaminants with chemicals and non-chemical constituents create severe environmental threat. Hence to compensate

these effects cheap natural resources named Citrus peels was used for present study.

Characterization of Citrus Peels:

Table No: 1 Determination of Moisture Content

Name	Wet weight (g)	Dry weight (g)	Moisture content (%)
Citrus medica linn	145	120	17.24
Citrus limon	150	130	13.33
Citrus limetta	130	100	23.07

Table No1 represents the moisture content of three varieties of Citrus peels. It is noticed that *Citrus limon* possesses greater moisture content than the other two varieties. This study relates with the study represented by Poonam ***et al.***, 2018.

Physical Characteristics of Tannery Effluent Before Treatment:

S.No	PARAMETERS	OBSERVATION
1	Appearance	Grey
2	Odour	Rotten egg smell
3	Total Hardness (unit)	1000
4	pH	8.0
5	Total Suspended Solids(mg/l)	2700
6	Total Dissolved Solids(mg/l)	12680
7	Electrical conductivity (micro mho/cm)	19507

Table No: 2 Physical Parameters of the Tannery Effluent Before Treatment

Table No 2 depicts the physical characteristics of tannery effluent before treatment collected from Ambur. It is noticed that, colour of the water was grey, and the odour was similar to rotten egg smell. Also, the total hardness, Total Suspended Solids, Total Dissolved Solids, Electrical Conductivity ranges were very high. These results suggest us that, if this waste water is left in any of the water bodies or in land, it will surely affect the living sources of the water, and even the humans. The unacceptable smell will create breathing issues in humans. Considering the increased dissolved solids, hardness, it predicts us that, for the treatment large quantities of the chemicals should be used which itself will create pollution. The present investigation is supported by M.N.Hossain *et al.*, 2019.

S.No	PARAMETERS	OBSERVATION (mg/l)
1	COD	3000
2	BOD	1500
3	Calcium	820
4	Magnesium	560
5	Chloride	6000
6	Sodium	2000
7	Sulphate	1500
8	Chromium	9
9	Oil and grease	12.75

Table No: 3 Chemical characteristics of the Tannery Effluent Before Treatment

Table No 3 represents the chemical parameters such as BOD, COD and minerals. It is noticed that the level of BOD and COD is greater which indicates that the water is unsuitable for the growth of the living organisms in water. Also, the level of mineral concentration was found to be greater which represents that the water is completely unsuitable for domestic purposes and even agriculture. The present finding relates with the finding of Tasneembano Kazi *et al.*, 2013. Looking in to the data all the physical and chemical constituent rates were found to be high with offensive smell and black in appearance. In case this effluent is exposed out without any treatment process, it has the capability to affect the surrounding environment sources.

Hence it was subjected for treatment using the citrus peels.

Treatment of Tannery Effluent using Citrus Peels

Since the collected tannery effluent shows higher rate of physical and chemical parameters, it was chosen for the treatment purpose. For the treatment Lemon species (*Citrus medica linn, Citrus limon, Citrus limetta*) was chosen and each was taken at different concentration ranging from 0.5, 3.0. 5.5, 8.0, 10.0 g/100 ml which varies from smaller to greater concentration.

Figure No: 1 Tannery Effluent after treatment using *citrus medica linn, Citrus limon, citrus limetta* (conc - 0.5, 3.0, 5.5, 8.0, 10.5g/100ml)

Figure No 1 represents the flask which was subjected to treatment process. By comparing the flask before and after treatment it is noticed for visualizing that colour of the effluent has changed which makes us understand that lemon peels are having the property of decolouration. The colour change was noticed in a greater level in the flask where *Citrus limon* peel powder was added. The present investigation was supported by Poonam *et al*., 2018.

Physical chemical Characteristics of Tannery Effluent after Treatment

Table no 4 represents the physical properties of the tannery effluent after treatment with *Citrus medica linn, Citrus limon, Citrus limetta* peel powder. The results indicate that as the concentration of *Citrus medica linn, Citrus limon, Citrus limetta* peel powder is increased for treatment process. The levels of physical parameters were decreased and the pH also has changed from alkaline to slightly acidic. That is 6.5 for 10.5g/100ml concentration of lemon peel powder and for *citrus limetta* peel powder the pH has been changed from alkaline to neutral that is 7.0 at 10.5g/100ml. The *Citrus medica linn* peel powder was not as effective in reducing the total hardness, TDS and TSS only slight variation is seen before and after treatment. The pH value also remained the same as 8.0 in both before and after treatment. Finally, the lemon peel powder has reacted with the tannery effluent and reduced the physical parameters such as hardness, TSS and TDS electrical conductivity.

Citrus peel variety	PARAMETERS					
	Appearance	Odor	Total hardness	pH	TSS (mg/l)	TDS (mg/l)
Citrus medica linn	Grey	Moderately Agreeable	1562	8.0	1989	10212
Citrus limon	Grey	Moderately Agreeable	992	6.5	1219	4659
Citrus limetta	Grey	Moderately Agreeable	1490	7.0	1429	9120

Table No 4 Physical Parameters of the Tannery Effluent After Treatment with *Citrus medica linn, Citrus limon, Citrus limetta peel powder*

Chemical Parameters of Tannery Effluent after Treatment with citrus varieties:

Citrus peel Variety	BOD 10.5g/100ml	COD	Calcium	Magnesium	Chloride	Sulphate	Chromium	Oil and grease (units)
Citrus medica linn	1438	2400	927	516	5807	1450	19	13.01
Citrus limon	980	1250	719	506	3592	800	0.9	12.02
Citrus limetta	1029	2273	746	382	1773	1020	15	11.99

Table No 5 chemical parameters of Tannery effluent after treatment with different Concentration of Citrus (*Citrus medica linn, Citrus limon, Citrus limetta*) Peel Powder

Table no 5 represents the chemical parameters of tannery effluent after treatment with *Citrus medica linn, Citrus limon, Citrus limetta* peel powder. BOD, COD analysis was performed after treating the tannery effluent using three varieties of lime at concentrations (0.5, 3.0, 5.5, 8.0, 10.5g/100ml). when the BOD and COD values were analysed it was found that after the treatment by *Citrus limon* peel powder at concentration of 10.5 g/100ml. the values has gradually decreased as BOD - 980g/l, COD - 1250g/l to a greater extent when compared to *Citrus limetta* peel powder (BOD - 1029g/l, COD- 2273g/l) and *Citrus medica linn* peel powder (BOD - 1438g/l, COD - 2400g/l).

Thus, it is evident that, the *citrus limon* peel powder has acted as a good adsorbent which has reduced the BOD, COD values. Mineral such as calcium, magnesium, chlorine, sulfate, chromium levels has decreased after treatment with *citrus limon* peel powder than the *Citrus limetta* and *Citrus medica linn* peel powder. Chromium, one of the mineral considered to be very dangerous to all lives also has been effectively removed using citrus limon peel powder. Thus, the *Citrus limon* peel powder has acted very effectively. The present findings are supported by Poonam *et al*., 2018.

FT IR Analysis of *Citrus limon* peel powder

Figure No: 2 depicts the graph of FT IR taken in the range of 400 – 4000 cm^{-1} for the *citrus limon* peel powder.

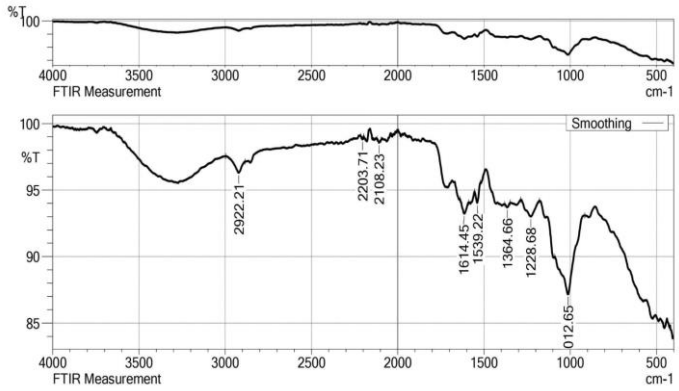

Figure No: 2 FT IR Analysis of *Citrus limon* peel powder

It is seen in the graph, wide and intense peaks among 3200 and 3600 cm^{-1} in both spectra due to the stretching vibrations of free of H bonded hydroxyl groups of phenols, alcohols, and carboxylic acids. The peaks observed around 2922.21 indicate the stretching vibrations of methylene, methoxy, methyl groups. The peak observed in the range of 1614.45 indicates C ≡ C stretching, the peak at 1539.22 indicates N-O stretching. The peak at 1364.66 indicates the OH bonding (alcoholic group) (Poonam *et al*., 2018).

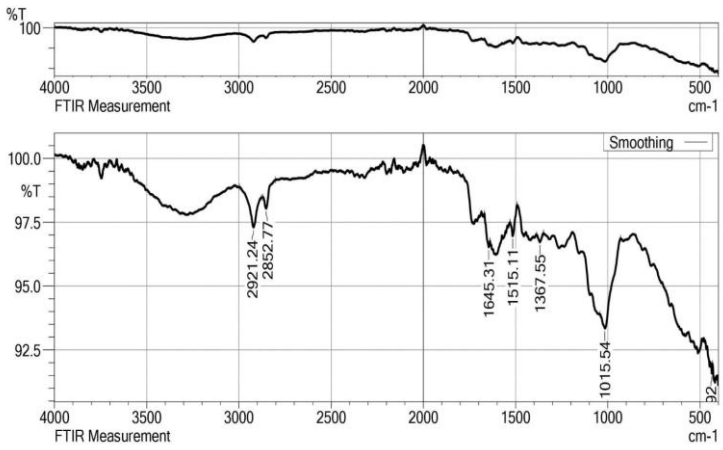

Figure No: 3 FT IR Analysis of *Citrus limetta* peel powder

Figure No: 3 depicts the graph of FT-IR taken in the range of 400 - 4000° c^{-1} for the *Citrus limetta* peel powder. It is seen in the graph, a wide and intense peak among 3746 – 3755 cm^{-1} represents the presence of - OH group which may be phenolic compounds. A sharp peak at 2921.24/ cm^{-1} is probably due to hydrogen bonded –OH stretching, wave no 1645.31 is assigned to the NH_2 in primary amines as a result of -NH_2 deformation. Peaks at wave no 1515.11 cm^{-1} indicates NH_2 in secondary amide, triazine compounds, NO_2 in aromatic nitro compounds. The peak at 1367.55 indicates aliphatic compounds (CH_3) and isopropyl groups (Amita Shakya *et al*., 2019).

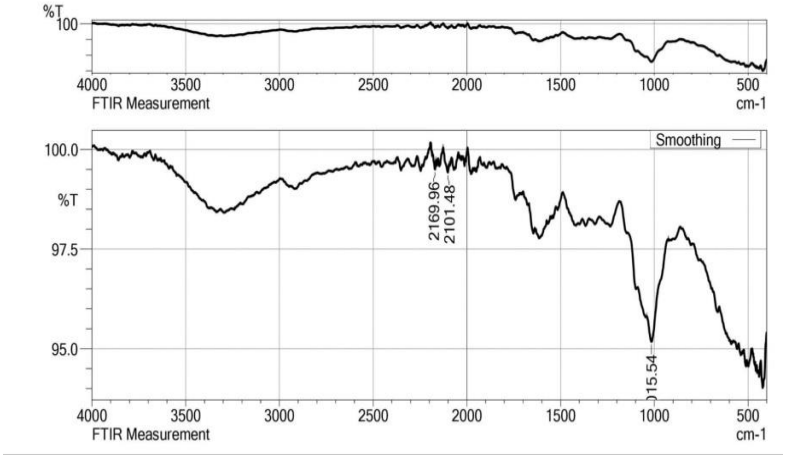

Figure No 4 FT IR Analysis of *Citrus medica linn* peel powder

Figure No: 4 depicts the graph of FT-IR taken in the range of 400 - 4000° c^{-1} for the *Citrus medica linn* peel powder. It is seen in the graph, a wide and intense peak at 2169.96/ cm^{-1} is probably due to symmetric and asymmetric C-H stretching of phenolics, peak observed at 2141.48 refers to–CN stretching characteristic of aromatic nucleus (Kumar *et al*., 2017).

From the above findings, it is evident that the citrus limon and citrus limetta peel has the predominant OH groups contributed by Phenol, alcohol and hydroxyl groups, which would have been the functional groups involved in reacting with the minerals present in the tannery effluent and hence reduced the pH, total hardness, TDS, TSS, BOD, COD and the concentration of minerals. But in case of *Citrus medica linn* the intensity peaks reflect OH group is less than citrus limon and citrus limetta and hence reduction in pH, total hardness, TDS, TSS, BOD, COD and minerals level was found to be lesser.

CONCLUSION:

Based on the finding of the current work, it could be concluded that *Citus limon*, *Citrus limetta*, *Citrus medica linn* can be used to reduce (or) control heavy metals from industrial effluent.

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